XVII. *On the mutual action of sulphuric acid and alcohol, with observations on the composition and properties of the resulting compound. By Mr.* HENRY HENNELL, *chemical operator at Apothecaries' Hall. Communicated by* W. T. BRANDE, *Esq. Sec. R. S.*

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THE following experiments were originally undertaken with the view of ascertaining the nature of that singular product of the distillation of sulphuric acid and alcohol, which has long been known in the pharmaceutical laboratory under the name of oil of wine, and which has generally been regarded by chemists as a modification of sulphuric ether. The results however of my enquiries have led me to very different conclusions, and induce me to regard it as a hitherto undescribed compound of sulphuric acid and carbon and hydrogen; the latter elements existing in the same proportions as in olefiant gas, and exerting a peculiar saturating power in respect to the acid. I have also ascertained that hydrocarbon, with an additional proportion of sulphuric acid, affords a compound which is capable of uniting with salifiable bases, and of forming a distinct series of products.

Of oil of wine.

As I originally considered the elements of oil of wine to be the same as those of ether, I endeavoured to ascertain their relative proportions by passing its vapour over red hot oxide of copper in a glass tube, in the apparatus contrived

for such decompositions by Dr. PROUT and Mr. COOPER, Trans. Soc. Arts XLI. p. 56. In these experiments I always obtained, along with the other products, a considerable proportion of sulphurous acid, and afterwards upon washing the contents of the tube with water upon a filter, it was of a bluish tint, and held sulphate of copper in solution; a result which I could not readily account for, as every precaution had been taken to free the oil of wine which I used from all adhering sulphurous and sulphuric acid.

I now added a few drops of the same oil of wine to a solution of muriate of baryta and gently heated the mixture, when not the slightest cloudiness was produced, although litmus paper indicated the existence of a free acid; but upon evaporating the mixture a precipitate fell, when it became concentrated, and on boiling it to dryness, a considerable quantity of sulphate of baryta was found in the residue: it became evident therefore that the sulphuric acid was in some state of combination which prevented its usual action upon tests, or that its elements were in some peculiar state of arrangement in the oil of wine.

To determine the quantity of sulphuric acid thus elicited, I boiled 200 grains of very carefully prepared oil of wine, free from all trace of acid, with a solution of caustic potassa to dryness; the residue was heated red hot and dissolved in water, the excess of potash being slightly supersaturated with dilute nitric acid; muriate of baryta was then added as long as it formed a precipitate, and 218,3 grains of sulphate of baryta were thus obtained. A repetition of this experiment gave the same results; so that we may conclude upon the presence of 74 grains of sulphuric acid in 200 of oil of wine.

In resuming the analysis of oil of wine by ignited oxide of copper, I found it necessary to mix it perfectly with the greater part of the oxide employed, otherwise, as in the first experiment, suphurous acid was formed in consequence of the perfect reduction of a portion of oxide, and the action of the metal thus reduced upon the sulphuric acid. With this precaution several experiments were performed, the results of which were very uniform, and as follows: 2.08 grains of oil of wine carefully freed from all adhering moisture by quicklime, were properly mixed with 200 grains of oxide of copper, and subjected with due precautions to a red heat, in the apparatus formerly adverted to: the products were 8.8 cubic inches of carbonic acid gas, and 1,54 grains of water, and these are equivalent to 0,171 of a grain of hydrogen, and 1,118 grains of carbon: 100 grains therefore of oil of wine would afford

Hydrogen	8,30
Carbon -	53,70
	62.

and the deficiency of 38 grains must be referred to sulphuric acid, a conclusion which is verified by the former experiment with solution of potassa, in which the proportion of that acid is shown to be 37 per cent. We may I think therefore conclude the above estimate to be near the truth, and the results, as respects the carbon and hydrogen, approximate nearly to the proportional quantities 6 and 1.

From the above experiment however we can only infer the composition of the hydrocarbon, which is combined with and neutralises the sulphuric acid, for in all the specimens of oil

of wine which I have examined, I have found a variable quantity of hydrocarbon held in solution, part of which spontaneously separates in a crystalline form when it has been kept for some time, or when exposed to cold, but the whole of which I have not yet devised any means of separating; this dissolved hydro-carbon, however, as future experiments will show, appears to be composed of single proportionals of its elements, we must therefore have recourse to other experiments to determine the actual weight of hydrocarbon in its neutral or atomic compound with sulphuric acid.

Having thus far made out the composition of oil of wine, I examined more carefully what had taken place during its action upon heated solutions of muriate of baryta and potash; in which case, as I have already observed, an acid had been formed not capable of precipitating baryta.

200 grains of oil of wine were placed in a flask with 5 or 6 ounces of water, and the flask set in a vessel of boiling water for an hour; precipitated carbonate of baryta was then added, and immediately dissolved with effervescence; about 90 grains of carbonate were required to neutralize the acid formed: the solution filtered and set to evaporate soon became acid, and sulphate of baryta precipitated. 200 grains more of oil of wine were treated in the same way, but instead of evaporating the baryta solution, it was precipitated by carbonate of potash; the potash solution evaporated at a temperature of 150° until it crystallized, remained perfectly neutral; the crystals were thin plates, not unlike chlorate of potash, greasy to the touch, very soluble in water and alcohol, burning when heated with a flame like that of ether, and leaving an acid sulphate of potash. A few grains of these

crystals were heated in a tube, when they fused, swelled up, and gave off a dense white vapour, which condensed into an oil-like fluid, smelling strongly of sulphurous acid; the residuary salt was an acid sulphate of potash.

The following experiments were now undertaken with a view of more accurately determining the composition of this crystalline salt.

20 grains of the crystals being heated to redness, left 10,56 grains of sulphate of potassa, equal to 4,8 sulphuric acid, 5,76 potash. 20 grains were dissolved in a solution of caustic potash, boiled to dryness, heated red hot, when cold dissolved in distilled water, the excess of potash saturated by nitric acid, and the solution added to one of muriate of baryta; 28 grains of sulphate of baryta were obtained, very nearly equal to 9,6 sulphuric acid; the salt therefore contained twice the quantity of sulphuric acid required to form a neutral sulphate with the potash, or two proportionals.

In order to ascertain the proportions of the remaining elements of the salt, 5 grains were heated with oxide of copper, 5,5 cubic inches of carbonic acid gas, and 1,4 grains of water were collected; several of these experiments were made with similar results; 20 grains of the salt had been found to contain 5,76 potash,

9,60 sulphuric acid.

5 grains therefore must have contained	1,44 potash.
	2,40 sulphuric acid.
5,5 cubic inches carbonic acid gas contain	0,699 carbon.
The water obtained was - - -	1,40.
	5,939 grains.

making an excess over the 5 grains employed of 939 of a grain. If this excess be oxygen furnished to hydrogen to form part of the water obtained, and such a view is confirmed by the loss of weight of the tube and its contents after the operation, it will give of hydrogen 0,1174 of a grain, and of water so formed 1,05 grains; this deducted from the whole quantity of water obtained, leaves 0,35 of a grain water of crystallization; 100 grains would therefore be composed of

Potash -	28,84
Sulphuric acid	48,84
Carbon -	13,98
Hydrogen -	2,34
Water -	7.

These numbers indicate nearly one proportional of potash, two of sulphuric acid, four of carbon and four of hydrogen; and it would appear that in these salts the four proportionals of carbon, with the four of hydrogen, are saturating one of sulphuric acid. I am not able at present to account for the difference between the quantity of water and a proportional number, every precaution having been taken in these experiments to insure accuracy. Several attempts were made to procure an anhydrous salt, but without success, in consequence of the facility with which these acids and other compounds decompose.

The resemblance of these salts to the sulphovinates, induced me to suppose they might be similar in composition, I therefore prepared some sulphovinate of potash. Its crystalline form was the same as that of the salt obtained from oil of wine, and upon examination it proved in all respects similar.

While preparing some of the sulphovinates, I was struck with the very great change produced in sulphuric acid by mere mixture with alcohol.

440 grains of sulphuric acid were mixed with an equal weight of alcohol of specific gravity ,820 ; the mixture when cold was diluted with water and saturated by carbonate of soda, partially dried, of which it required for saturation 398 grains, while 440 grains of sulphuric acid not mixed with alcohol saturated 555 grains of the same carbonate of soda, so that $\frac{2}{7}$ of the acid had been saturated by the alcohol.

440 grains of sulphuric acid mixed with its own weight of alcohol, as before, and then poured into a solution of acetate of lead, 542 grains of sulphate were precipitated. The same quantity of sulphuric acid unchanged by alcohol gave 1313 grains of sulphate of lead; thus $\frac{4}{7}$ of the sulphuric acid had lost its power of precipitating oxide of lead from its solutions; it had in fact been converted into sulphovinic acid.

M. VOGEL, who has particularly described some of these salts, and I believe also M. GAY LUSSAC, have supposed that this loss of saturating power arises from the formation of hyposulphuric acid, and that the hyposulphates, and sulphovinates, only differ in the latter containing some ethereal oil, which in some way acts the part of water of crystallization. It is evident that the properties of oil of wine cannot be thus explained; and it appears to me more probable that the power of combination which hydrocarbon is shown to be possessed of in oil of wine, is effective in neutralising half the acid of the salts formed from it, as before described.

It only now remains to examine the hydrocarbon in the states in which it has been obtained separate from its combinations.

When oil of wine is heated in a solution of potash, or if heated in water merely, the excess of hydrocarbon above that necessary to constitute the acid, forming the salts I have described, is liberated in the form of an oil, not unlike in appearance castor oil, having but little fluidity when cold, and in some cases partially crystallizing. When gently heated it is beautifully bright, and of an amber colour; the vapour has an agreeable pungent and aromatic smell; it evaporates at a temperature a little above that of boiling water; burns with a brilliant flame, throwing off some carbon; its specific gravity is about 9, water being 10; it is insoluble in water, very soluble in ether, somewhat less so in alcohol.

Several analytical experiments were made upon this substance with similar results. When decomposed by oxide of copper, 0,72 of a grain gave 4,85 cubic inches of carbonic acid gas and ,85 of a grain of water; 4,85 cubic inches of carbonic acid gas are equal to 0,6164 of a grain of carbon, and the 0,85 of a grain of water to 0,09444 of a grain of hydrogen; 100 parts should therefore be composed of

Carbon 85,61
Hydrogen 13,116.

There is here some trifling loss; if that be supposed to be hydrogen, this oily matter is precisely similar in the proportions of its elements to olefiant gas.

The crystals which spontaneously separate from oil of wine were next examined; they were prismatic, and resembled precisely in all their characters, except their solid form, the fluid substance just described. They fused at a temperature a little above that of boiling water. After purifying a portion by pressing them in blotting paper, to remove

any adhering oil of wine, several experiments were made upon quantities of a grain each; 6,46 cubic inches of carbonic acid gas and 1,21 grains of water were obtained; the 6,46 cubic inches of carbonic acid equal ,82106 of a grain of carbon, and the 1,21 grains of water equal ,13444 of a grain of hydrogen.

The carbon and hydrogen are here very nearly in single proportionals, but there is great loss, I believe: this may be partly attributed to oil of wine still adhering, but of that I am not at present able to satisfy myself, my stock of crystals being exhausted.

On mentioning these results to Mr. FARADAY, he gave me some sulphuric acid which had been exposed to olefiant gas, during some of his experiments on the products of the decomposition of oil by heat. It had absorbed about 80 times its volume of the gas, acquired a deep brown colour, and a smell resembling oil of wine. It was saturated by carbonate of potash carefully evaporated to dryness, and the dry mass digested in alcohol. A small quantity of a salt was obtained from the alcoholic solution having the crystalline form and general characters of the salts I have been describing.

Thus it would appear that hydrocarbon constituted of single proportionals, or 6 carbon and 1 hydrogen by weight has the power of combining with sulphuric acid; and that whether it be evolved and then combined, as in the case of olefiant gas, or its elements separated from other compounds, as from alcohol, it forms precisely the same combination, sulphovinic acid. It further appears, that oil of wine is a perfectly neutral compound of sulphuric acid and hydrocarbon, and that it is resolvable by various processes into sulphovinic acid, during

which it loses hydrocarbon, and acquires a saturating power equivalent to only half the natural power of the sulphuric acid it contains. The remaining hydrocarbon enters with it into saline combinations, and is there equivalent in saturating power to the quantity of base taken up. The proportions of hydrocarbon which in this way replaces bases being four proportionals, or 24 carbon, 4 hydrogen.